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Surface Analysis of Anodized Aluminum Panels that have
been Painted, Bead Blasted, Cleaned, and Treated
with a Chemical Conversion Coating.

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Abstract

Aluminum panels were prepared to simulate the process an aircraft undergoes for repainting. This process consisted of stripping the original paint down to the anodized aluminum by bead blasting with polymethyl methacrylate (PMMA), cleaning the surface, corrosion removal, followed by a chemical conversion coating. The chemical conversion coating was applied on panels from 0 to 15 minutes. The surface analysis was performed using a Surface Science Instrument Model 501 ESCA. The surface analysis has shown several interesting phenomena that occurred on the panels. The phenomena includes non uniformity of the surfaces, changes in the atomic concentrations, and changes in the organic layers. Changes in the chemical states of the elements vs the chemical conversion coating times were also detected. The non uniformities were present in both the elemental surveys and the high resolution scans. The elemental surveys showed that the atomic percent of the elements (especially Cr) changed with the chemical conversion coating time. The high resolution scan of carbon showed that a layer of PMMA was left on the surface after bead blasting. After cleaning and applying the chemical conversion coating compound, the organic layer consisted of mainly hydrocarbons and alcohols/ethers, however, areas with slight amounts of PMMA were also detected. The high resolution scans of the aluminum peaks showed that the chemical states of aluminum changed with the chemical conversion coating time. That is, the surface aluminum changed from an unoxidized aluminum to

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a mixture of an oxide and a possible complex oxyfluoride surface at longer coating times.

Introduction

The surface preparations for repainting an aircraft have relied heavily on the use of volatile organic compounds such as Methyl Ethyl Ketone (MEK). The safety and environmental concerns of these compounds are rapidly limiting their use. The elimination of these compounds from the repainting process will effect the properties of the surface to be painted. These effects will be most notable in the removal of the organic contaminants, the quality of the chemical conversion coatings, and the adhesion of the environmentally compliant (low VOC) primers and topcoat paints. This surface study was undertaken to determine some of the possible changes that will occur.

Experimental Procedure

One square foot panels of 2024 T6 chromic acid anodized aluminum were used as the base alloy. The panels were primed and painted with a FMS 1058 and TTP-2760 primers and a MIL-C-85285 paint. The primers and paint were allowed to cure. The painting of the panels was preformed to simulate the aircraft skin prior to arrival at OO-ALC.

The painted test panels were subjected to the process that an aircraft currently undergoes for repainting at OO-ALC. The first step in the repainting process is to remove the old paint. This was accomplished by a plastic medium blast (PMB) in accordance with the T.O. 1-1-8. The plastic blast medium used was qualified to MIL-P-85891 type V. For the type V medium, MIL-P-85891 calls for a MEK or similar solvent wipe. The solvent used for the wipe was qualified to FMS-2004A. After the solvent wipe, the panels were scrubbed with a alkaline cleaner. A corrosion removal compound qualified to MIL-C-38334 was then applied to the surface in accordance to the T.O. The final step prior to repainting was the application of a chemical conversion coating qualified to MIL-C-81706. In this study the chemical conversion coating compound was applied to the panels from 0 to 15 minutes. A four inch square was cut from the center of the test panels for the surface analysis. There were three locations analyzed per sample.

The surface analysis technique used to analyze the panels was Electron Spectroscopy for Chemical Analysis (ESCA). The ESCA used

was a model 501 Surface Science Instrument. ESCA is also known as X-Ray Photoelectron Spectroscopy (XPS). The ESCA uses an Al $K\alpha$ X-ray source to knock out the photoelectrons. Each element has characteristic photoelectron energies which allows the elemental surface composition to be determined. The chemical state of the surface elements are determined by comparing subtle shifts in the photoelectron energies. These shifts are caused by the oxidation state of the element, and are evident in high resolution scans. The analyses were performed with the following parameters: The pressure in the analytical chamber was 1×10^{-9} Torr. The pass energy was set at 100 eV for the elemental surveys, and 50 eV for the high resolution scans. The 1000μ spot was used for each analysis. The flood gun was turned on with an energy of 5 eV. The flood gun was required to reduce the effects of surface charging.

Chemical fingerprints of the anodized aluminum, PMB, cleaners, corrosion removal compound, and the chemical conversion coating compound were acquired. The ESCA fingerprints included elemental surveys and high resolution scans of key elements. The atomic percent of the elements were calculated from the elemental surveys using the instruments internal software program. The high resolution scans were performed on aluminum (Al 2p peak), chromium (Cr 2p₁ and Cr 2p₃ peaks), carbon (C 1s peak), and oxygen (O 1s peak). A curve fitting routine was used to determine the energy values of peaks in the high resolution scans. The hydrocarbon peak in the C 1s scan was adjusted to the reference value of 284.6 eV. The fingerprints were obtained for comparison to elemental surveys and high resolution scans that were taken during various steps in the repainting process.

Results and Discussion

The elemental and chemical fingerprints of the compounds used in the repainting process were obtained. These fingerprints provided information on the origin of the residues left on the panels' surface. The plastic blast medium was determined to be polymethyl methacrylate (PMMA). The blast medium was characterized with nuclear magnetic resonance (NMR), infrared spectroscopy (IR), and ESCA. The alkaline cleaner was found to leave a carbon film consisting of hydrocarbons and an alcohol/ether. The corrosion removal compound was found to contain an ether using Fourier Transform Infrared Spectroscopy (FTIR). The corrosion removal compound left a carbon surface residue that corresponds to an ether. The C 1s peak for the cleaning compounds, the

corrosion removal compound, and the PMMA contain a peak that corresponds to alcohols/ethers. This interference between these compounds did not allow for the exact determination of the origin of the alcohols/ethers on the final panels. However, the PMMA had a peak in the carbon high resolution scan that is not common with the other compounds. From this peak it was determined that there was PMMA on the chemical conversion coated panels.

The elemental surveys on the conversion coated panels detected the presence of the following elements: carbon, oxygen, nitrogen, silicon, sulfur, phosphorus, iron, calcium, fluorine, chromium, and aluminum. The elemental fingerprint for the solvent, alkaline cleaner, and corrosion removal compound account for P, and Si elements. The Cr, F, Fe, and N are from the chemical conversion coating compound. The Fe was only seen on the panels that had the chemical conversion coating compound applied for 10 and 15 minutes. The Al is from the base alloy. To determine the origin of the carbon on the surface the oxidation state had to be determined. This was done in the high resolution scans of the C1s peak.

The high resolution fingerprint for the C1s peak, of the bead blast medium, is shown in Figure #1. The peak locations [1] fit those of the functional groups in PMMA. The peak ratios of 3:1:1 also match that of PMMA. The high resolution scans for the O1s peak also matched the oxygen ratio for PMMA. To determine if bead blasting leaves a residue, a panel was analyzed after bead blasting, but prior to the solvent wipe. The C1s peak on the bead blasted surface showed an increase in the full width at half maximum of the peaks, a surface charging phenomena, and an increase in the percentage of the hydrocarbon on the surface. The peak broadening may be due to a combination of the surface roughness, and the surface charge. Using the peak that corresponds to the ester in PMMA, the surface of the carbon film was calculated to contain 49% PMMA. The remainder of the carbon was a hydrocarbon. After the solvent wiping, alkaline scrub, and the application of the corrosion removal compound the percent of PMMA in the carbon peak was reduced. However, the cleaning process added a carbon film consisting of an alcohol/ether on the surface. Additional studies on the PMMA and the cleaning ability of solvents will be presented in future work. The chemical conversion coating compound was applied to the cleaned panels for 5, 10, and 15 minutes. After the application of the conversion coating compound, PMMA and alcohols/ethers were detected. The chemical conversion coated panels had three distinct characteristics: (1) there was a non uniformity of the coating, (2) the atomic percent of the

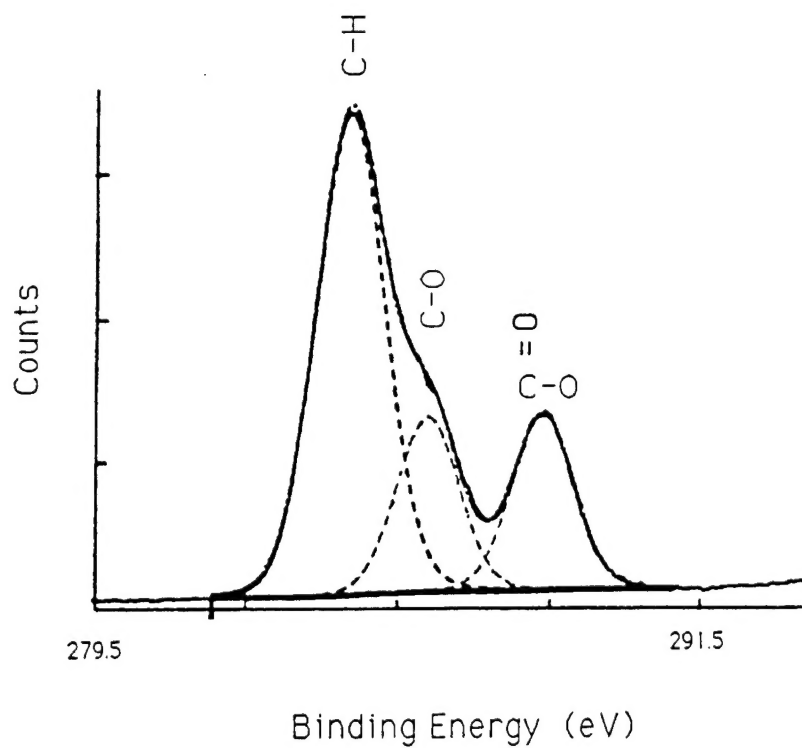


Figure #1 C1s high resolution scan of
the bead blast medium.

elements changed with the coating time, and (3) the oxidation state of aluminum changed with the application time of the chemical conversion coating compound.

For a particular application time of the chemical conversion coating compound the oxidation state of chrome varied. High resolution scans of the Cr 2p₁ and Cr 2p₃ peaks were used to determine the oxidation state of the chrome. The chrome peak energies were found to correspond to literature [2,3] values for Cr+3 and Cr+6. There was no set ratio in the amount of Cr+3 to Cr+6 as found in a similar system analyzed by H. A. Katzman [4] et al. The ratio of the Cr+3 to Cr+6 was found to vary widely from location to location. Several articles [5,6] in the literature have found other non uniformities in chemical conversion coating films.

The atomic percent of Cr, F, Fe, and N on the surface changed with the application time of the chemical conversion coating compound. These elements were also detected in the fingerprint of the conversion coating compound. Figure #2 is a graphic representation of the average atomic percent of the elements vs the application time. The error bars represent the standard deviation. Iron was detected only on the panels with application times of 10 and 15 minutes.

The chemical state of the aluminum on the test panels changed with the application time of the chemical conversion coating compound. To determine the chemical state of the Al2p peaks their energy values were compared to literature [3, 7, 8, 9] values. The chemical state of the aluminum on the surface of the 5 minute panel consisted of mostly Al⁺⁰ (Figure 3a). Sunderland [10] found the surface aluminum in this state for a similar system. The 10 minute panel contained Al⁺⁰ and Al₂O₃ (Figure 3b). The aluminum oxidation state for the 10 minute sample differs from the 5 minute sample by an increase in the percent of Al₂O₃. The 15 minute panel contained Al⁺⁰, Al₂O₃, and a third peak at a higher energy (Figure 3c). This third peak was located between the Al₂O₃ peak location and that of AlF₃. No literature data was found that could give a chemical composition to this peak energy. However, this peak could correspond to an oxyfluoride that had been mentioned in other publications [5, 11, 12].

In the reaction chemistry for the chemical conversion coating presented in other publications [4, 13] one of the reactants is AlF₃. A panel that had not been painted and prepared for repainting was used for a comparison to the test panels. This panel had the chemical conversion coating compound applied for 5 minutes. The high resolution scan for the Al2p peak (Figure #3d) detected only Al₂O₃ and AlF₃. In the panels prepared for repainting, a peak located at the AlF₃ energy was not

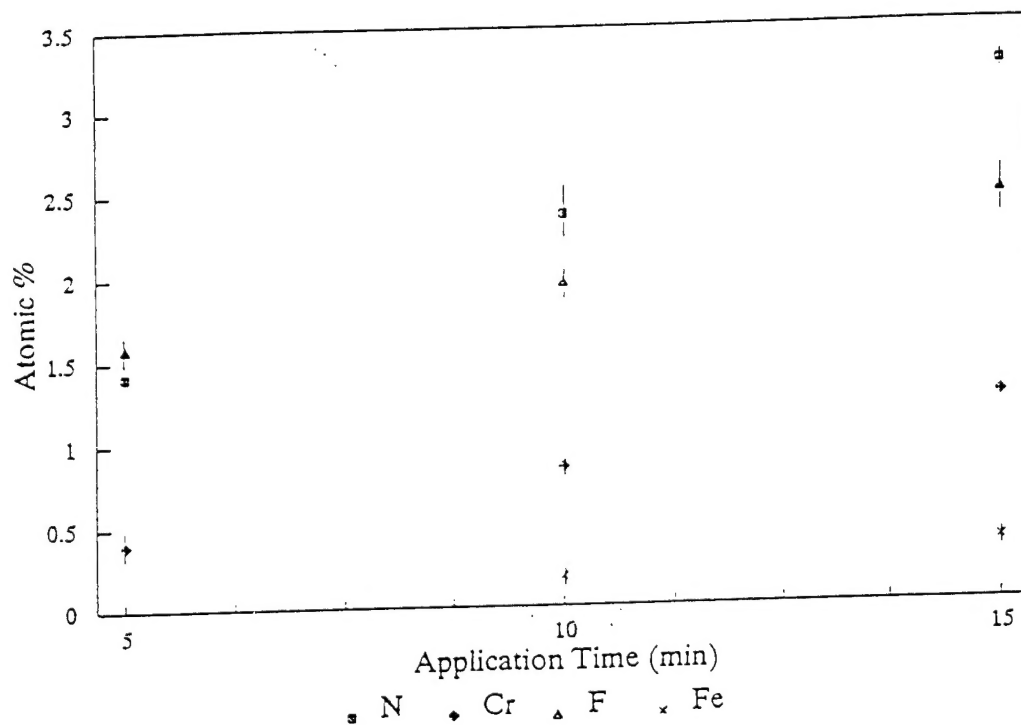


Figure #2 The surface atomic percent for chrome, fluorine, iron, and nitrogen vs the application time of the conversion coating compound. The error bars represent the standard deviation.

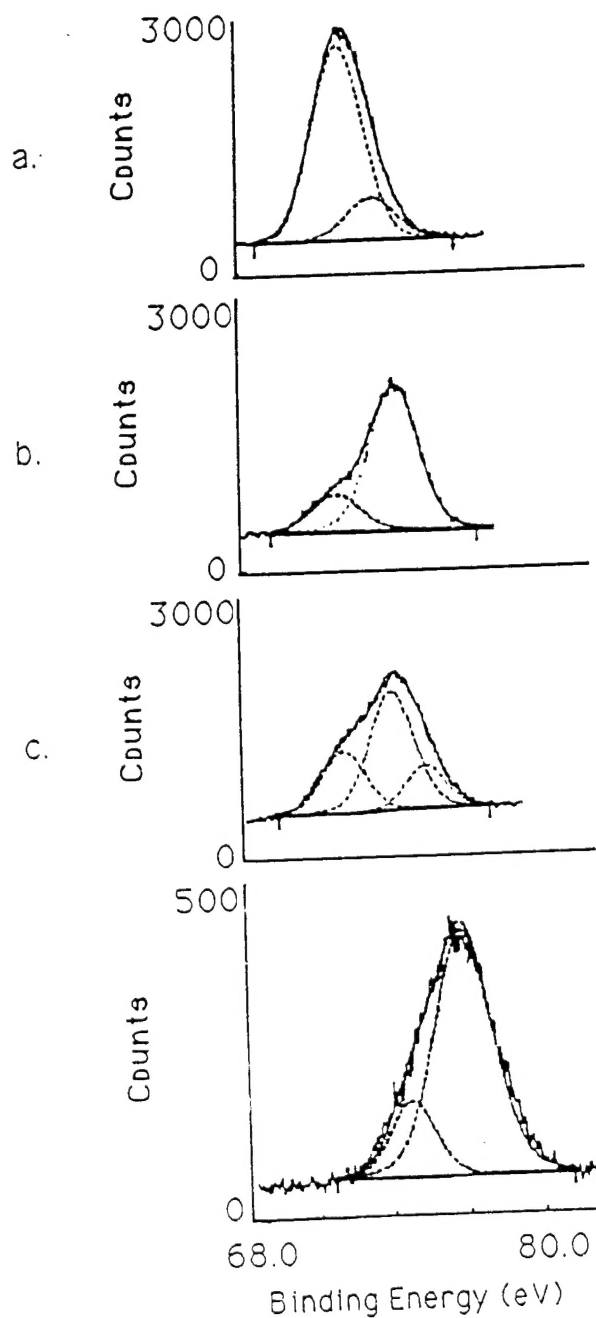


Figure #3 High resolution scans of the $\text{Al}2p$ peak vs application time of the conversion coating compound. a) 5 min. panel containing mostly Al^{+0} b) 10 min panel contains Al^{+0} and Al_2O_3 c) 15 min. panel contains Al^{+0} , Al_2O_3 , and a possible oxyfluoride d) 5 min. application of the chemical conversion coating compound on an anodized panel that did not undergo the repainting process. Contains Al_2O_3 and a peak near the energy of AlF_3 .

detected. This demonstrated that the preparation for repainting does have an effect on the chemical conversion coating.

Conclusions

This surface study of the repainting process has demonstrated four distinct results. First, the bead blast medium was not totally removed by the cleaning process. Second, the atomic percentage of chemical conversion coating elements on the surface was dependent on the application time. Third, the high resolution scans showed that the chrome was in the trivalent and hexavalent states. Fourth, the chemical state of the aluminum changed with the application time of the conversion coating.

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